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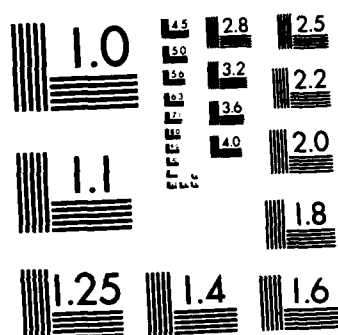
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TECHNICAL REPORT NO. 16

EXPERIMENTAL PICOSECOND TRANSIENT SPECTRA

FOR I_2 PHOTODISSOCIATION IN LIQUIDS

BY

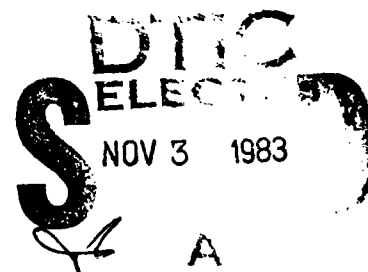
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ABSTRACT

→ After dissociative excitation into the A state the molecular dynamics of the I₂ reaction in solution are followed by picosecond transient electronic absorption spectroscopy. The time scale of the transient spectra varies considerably among different solvents. For the same reaction process, observation at higher photon energy gives longer transient spectral times. The results appear consistent with a model in which the major determinant of the observed time scale is due to vibrational (or possibly electronic) decay after recombination and inconsistent with a model in which the time scale is dominated by recombination time. ←

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I. INTRODUCTION

This letter experimentally investigates the liquid phase dynamics of the chemical reaction sequence involving I_2 photodissociation, solvent caging, radical recombination to form a new highly vibrationally (and perhaps electronically) ¹ excited I_2 molecule and the subsequent decay of its internal energy.

The photodissociation of I_2 has been frequently studied in the liquid phase, as it is one of the simplest chemical reactions, the same diatomic being both reactant and product. Earlier experimental work²⁻⁹ clearly indicates that much of the important molecular dynamics in this solution reaction occurs on the tens to hundreds of picosecond time scale. Two very different mechanisms have been proposed to account for the experimentally observed time scale for the transient electronic absorption. The first^{2,8} is that the time scale mainly represents the recombination time for the I atoms to reform I_2 molecules. The second, proposed more recently by us,^{5,6,9} and by Nesbitt and Hynes,^{10,11} with related ideas also expressed by Troe,¹² and by van den Berg,¹³ is that recombination is relatively quick and that the time scale is dominated by the time for vibrational decay of the newly formed I_2 . In this letter we experimentally test these alternative hypotheses.

II. EXPERIMENT

The theoretical interpretation of most previous picosecond experiments^{2-4,7,8} has been made difficult by the possible role of predissociation (or second photon absorption) by the B state which is presumably reached by initial pumping with green light. Therefore, we use a red 680 nm source (dye laser with DCM dye)¹⁴, to excite the I_2 molecules into the A state, a dissociative transition free from the predissociation complexity associated with the previous picosecond experimental studies,^{2-4,7,8} but at a cost of a reduction of a factor ~20 in absorption cross-section.¹⁵ A schematic diagram of the experimental system is shown in Fig. 1. An argon-ion laser (Spectra Physics, model 171) synchronously pumps in parallel two dye-lasers (Spectra Physics, model 375), each producing a train of ~8 ps FWHM pulses, separated by ~4 ns. The jitter between pump and probe pulses limits the time resolution of our measurements to ~20 ps.

In order to achieve the sensitivity needed to detect the very weak¹⁵ I_2 A state absorption, a multiple radio and audio-frequency modulation system is used.¹⁶ By processing the signal information initially in the radio-frequency regime much of the intrinsic laser noise is avoided. The pump and the probe beams are modulated at two different radio-frequencies (4.45 MHz and 11.2 MHz respectively) and the signal is observed at the difference frequency with an AM radio receiver. In addition the pump beam is audio-modulated at 400 Hz and the signal is synchronously detected at that frequency. This detection system, which is described in more detail elsewhere,¹⁶ provides a very sensitive technique for extracting weak signals from noise. In addition, this technique strongly discriminates against pump and probe beams, as well as against electrical pick-up from their modulating electronics. Even further rejection against the pump beam is achieved by placing an optical bandpass filter in front of the photodiode. It should be noticed that the sign of the transient signal is lost during signal processing in the receiver;

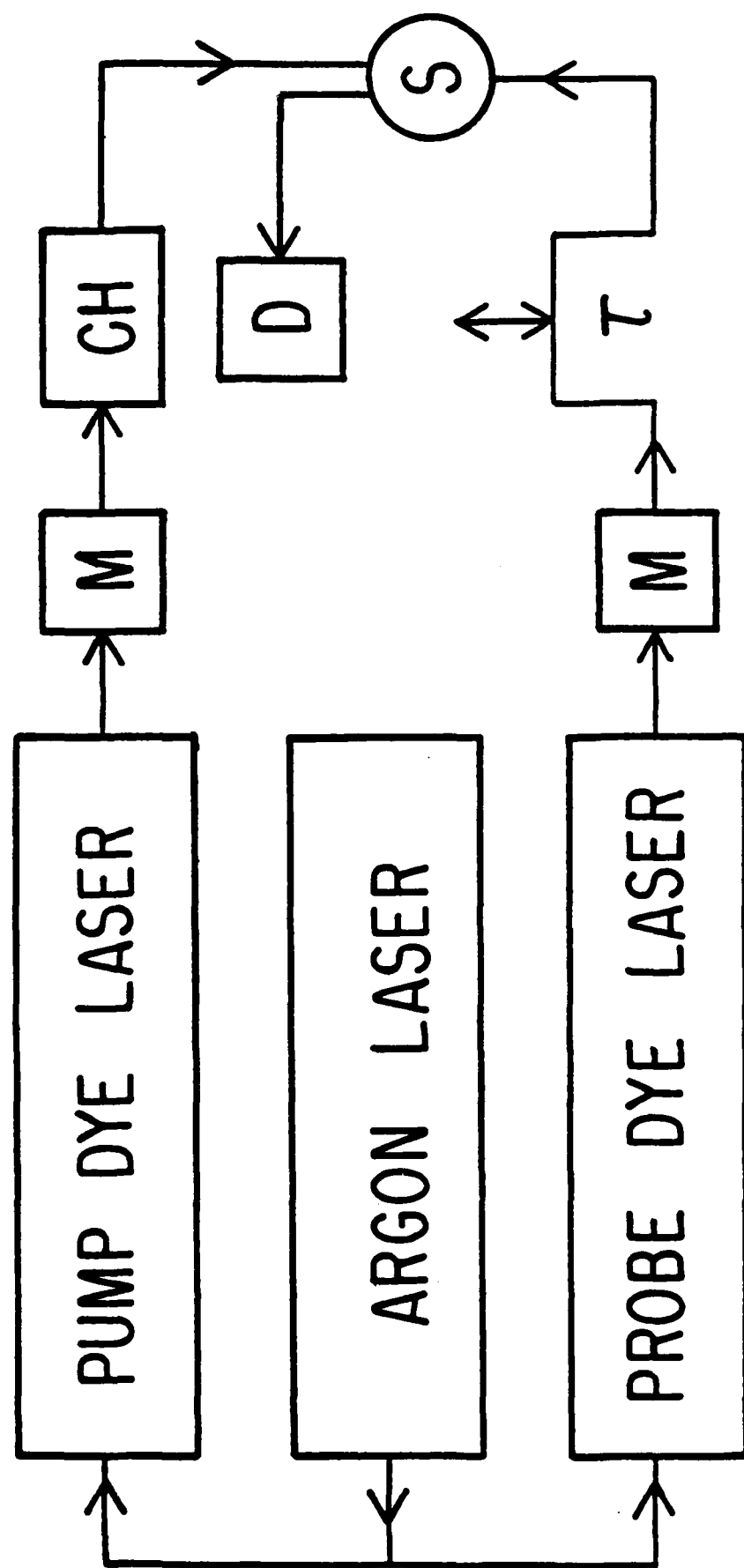


Figure 1.

Picosecond transient electronic absorption spectrometer. M indicates a megahertz electro-optical modulator, CH is a mechanical chopper, τ is the optical delay, S is the sample, and D the photodiode detector. The probe beam is polarized perpendicularly with respect to the pump beam.

therefore, we are presently not able to differentiate between induced absorption and induced bleaching.

Since the energy per pulse is in the nJ range, in order to achieve sufficient excitation our sample region is a small confocal volume at the focus of microscope objectives (American Optical, infinity corrected, power 6X) in both the pump and the probe beams which are collinear but traveling in opposite directions to avoid non-linear mixing of the probe and pump carrier frequencies in the photodiode. The reaction solution is rapidly pumped through the confocal volume inside a small capillary. The pump and probe power at the sample is typically on the order of 20 mw. The inner diameter of the capillary is ~ 1 mm (this slightly restricts our time resolution due to the counter-propagating geometry) and the sample temperature is between 296 and 304 K.

Reagent grade I_2 , ethylene glycol, cyclohexane and cyclohexanol are used without further purification. Carbon tetrachloride is of spectroscopic grade. The solutions are saturated in iodine as shown in Table I, except for measurement at 630 nm where the concentration is cut by half for the ethylene glycol solution to improve the signal to noise ratio. The wavelengths are checked prior to data collection with a calibrated monochromator. After passing through the sample, the probe beam is diverted by a beamsplitter or a polarizer onto a photodiode (EGG, model DT-110).

Table I. Concentration of iodine in saturated solution for various solvents at 25°C.

solvent	concentration $g\ l^{-1}$
Ethylene glycol	~ 12
Cyclohexanol	~ 35
Cyclohexane	~ 27
CCl_4	~ 29

Since cross-polarized light is used to pump and probe the sample, one may expect rotational motion of the molecules to contribute to the transient spectra. This orientational relaxation is expected to be fast^{2,17} and should not significantly affect our data.

III. RESULTS AND DISCUSSION

The transient absorption spectra for iodine in ethylene glycol, cyclohexane, cyclohexanol, and carbon tetrachloride as a function of time for three different probe wavelengths are shown in Fig. 2. The pump wavelength is fixed at 680 nm, while the probe wavelength is at 630 nm, 650 nm, or 710 nm. The results are summarized in Table II. Note that we could obtain no useful data for CCl_4 at 630 nm, possibly due to the effect of complexes or impurities. The raw data are corrected by taking the square root of the signal, to account for the quadratic response of the receiver.

The following general observations can be made:

- (1) For a given solvent, observation at a higher photon energy gives longer spectral time scales, at least for cyclohexane and CCl_4 . The time scale of the transient spectra for cyclohexanol and ethylene glycol at ~ 27 ps FWHM is identical and nearly instrument limited (~ 20 ps) at all probe wavelengths.

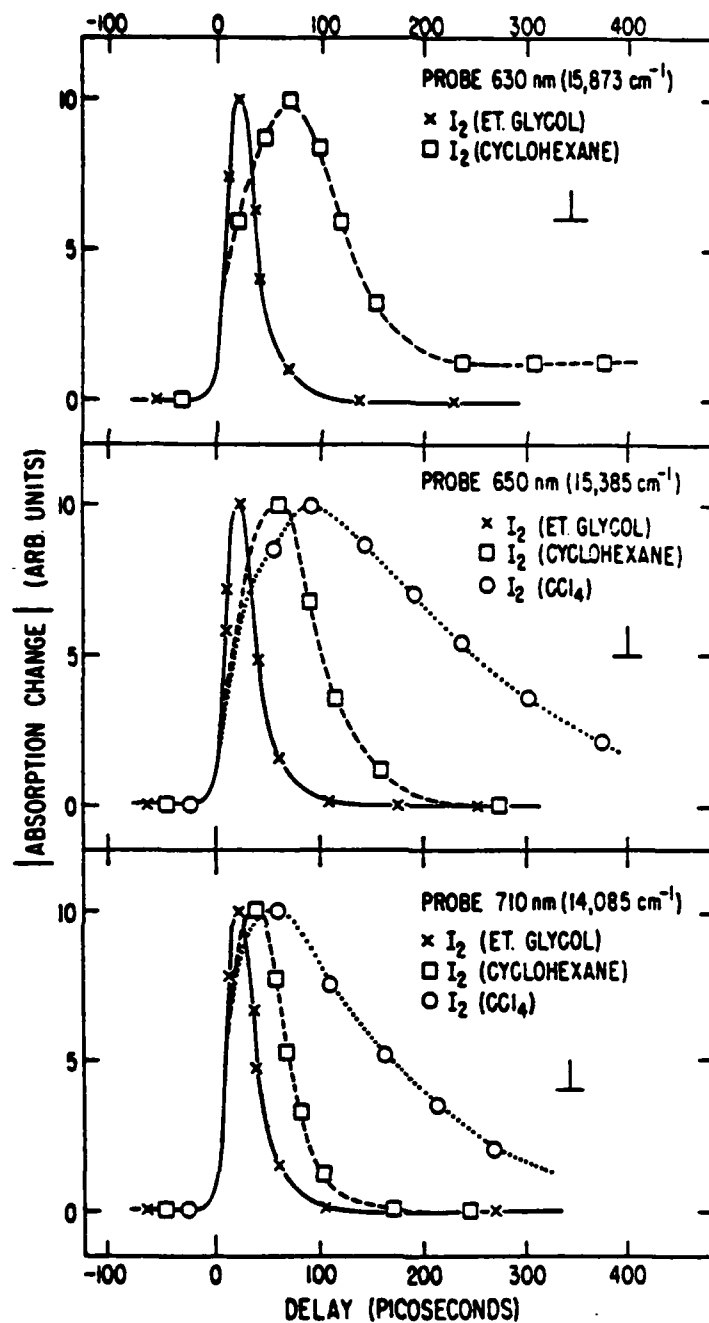


Figure 2.

Experimental transient electronic absorption spectra for I_2 photodissociation in ethylene glycol, cyclohexane and in chloroform at three different probe wavelengths (630 nm, 650 nm and 710 nm). Pump wavelength is 680 nm. Note that the time scale of the observed absorption change increases with probe photon energy. Cyclohexanol has the same transient spectra as ethylene glycol; for clarity it is not shown here.

Table II. *Transient electronic absorption time for I₂ photodissociation reaction in various solvents (FWHM in picoseconds). Data have been corrected for quadratic response of the detection system.*

Solvents	Probe wavelength in nm.		
	630	650	710
Ethylene glycol	27 ± 3	27 ± 3	27 ± 3
Cyclohexanol	29 ± 3	29 ± 3	29 ± 3
Cyclohexane	110 ± 10	95 ± 10	65 ± 10
CCl ₄	a	240 ± 20	180 ± 20

a) No useful data obtained.

(2) For a given probe wavelength, the time scale of the transient spectra is fast in ethylene glycol and cyclohexanol, intermediate in cyclohexane, and slow in CCl₄.

Both sets of observations can be theoretically rationalized as follows:

(1) The dependence of the observed time scale of the transient electronic spectra on the probe wavelength may be used to test the alternative mechanisms proposed as the explanations for the observed transient spectral time scale. If the time for the I atoms to recombine were the major cause of the delay for the electronic absorption, then observation at any probe wavelength should show this time delay caused by recombination. Since, as shown in Fig. 2, there is a large time scale change with probe wavelength for CCl₄ and cyclohexane (the instrumental time resolution would mask any change for ethylene glycol and cyclohexanol), we can rule out recombination time as the dominant mechanism, at least for the reactions initiated through the A state as tested here.

(2) The change in time scale with different solvents at a given probe wavelength can be correlated with the nature of the solvent^{5,6,9,18} as shown in a molecular dynamics simulation.¹⁹⁻²² Hydrogen bonding, as in ethylene glycol and cyclohexanol, is expected to produce a broad distribution in hindered translational and rotational frequencies of the solvent, in the range of the vibrational frequencies of the vibrationally excited I₂, quickly relaxing them as we observe. In contrast, molecular dynamics calculations^{9,18} show that the distribution of frequencies in liquid CCl₄ has a low overlap with the range of relaxing I₂ frequencies, and therefore one would expect, as observed, a longer time scale for the electronic transient spectra of I₂ photodissociation in CCl₄ if vibrational relaxation were the dominant mechanism in terms of time scale.^{5,6,9-11,23-26}

With the advent of new infra-red dyes,²⁷ we are presently probing at longer wavelengths. Our preliminary results²⁸ confirm the good correlation between experimental and theoretical spectra.

Three important caveats should be kept in mind. The first is that our transient signals could also reflect the presence of iodine atoms or molecules complexed with solvent molecules.^{3,8,29-34} In fact, for certain solvents at certain wavelengths (for example CCl₄ at 630 nm) we observe slower signal components which make accurate measurement of fast decays difficult or impossible. The second caveat is that the pathway from initial A state to final X state involves at least one interelectronic state transition whose details are unknown, and may involve other intermediate states as well.¹ The third caveat is that there might be differences in mechanism, for example involving predissociation, when I₂ is dissociated in the B state

region.^{2-4, 7, 8}

IV. CONCLUSION

Transient electronic spectra for the I_2 photodissociation reaction initiated through the directly dissociative A state have been measured as a function of the nature of the solvent and of probe photon energy. The results indicate that the previous interpretation of the characteristic time scale as being due to the time for recombination is incorrect. A more likely cause is the time required for vibrational (and perhaps electronic) decay of the already recombined molecules.

V. ACKNOWLEDGMENT

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1. P. B. Beeken, E. A. Hanson, and G. W. Flynn, "Photochemical and photophysical dynamics of I_2 isolated in a rare gas cage," *J. Chem. Phys.*, vol. 78, p. 5892 (1983).
2. T. J. Chuang, G. W. Hoffman, and K. B. Eiseenthal, "Picosecond studies of the cage effect and collision induced predissociation of iodine in liquids," *Chem. Phys. Lett.*, vol. 25, p. 201 (1974).
3. C. A. Langhoff, K. Gnädig, and K. B. Eiseenthal, "Picosecond laser studies of the photodissociation of I_2 - aromatic complexes and the formation of I atom-aromatic complexes in solution," *Chem. Phys.*, vol. 46, p. 117 (1980).
4. C. A. Langhoff, B. Moore, and W. Nugent, "Viscosity dependence of iodine recombination," in *Picosecond Phenomena II*, ed. R. Hochstrasser, W. Kaiser, and C. V. Shank, p. 249, Springer-Verlag, Berlin (1980).
5. P. Bado, P. H. Berens, J. P. Bergsma, S. B. Wilson, K. R. Wilson, and E. J. Heller, "Picosecond dynamics of I_2 photodissociation," in *Picosecond Phenomena III*, ed. K. B. Eiseenthal, R. M. Hochstrasser, W. Kaiser, and A. Laubereau, p. 260, Springer-Verlag, Berlin (1982).
6. P. Bado, P. H. Berens, and K. R. Wilson, "Picosecond dynamics of solution reactions," in *Picosecond Lasers/Applications*, ed. L. S. Goldberg, vol. 322, p. 230, Proc. Soc. Photo-Optic. Instrum. Engin., Bellingham, WA (1982).
7. C. A. Langhoff, B. Moore, and M. DeMeuse, "Diffusive and nondiffusive time scales in the dissociation and recombination of I_2 in linear alkanes," *J. Am. Chem. Soc.*, vol. 104, p. 3576 (1982).
8. D. F. Kelley and P. M. Rentzepis, "Predissociation and geminate recombination kinetics of I_2 in liquid Xenon and CCl_4 ," *Chem. Phys. Lett.*, vol. 85, p. 85 (1982).
9. P. Bado, P. H. Berens, J. P. Bergsma, M. H. Coladonato, C. G. Dupuy, P. M. Edelsten, J. D. Kahn, K. R. Wilson, and D. R. Fredkin, "Molecular dynamics of chemical reactions in solution," in *Proceedings of the International Conference on Photochemistry and Photobiology*, ed. A. Zewail, Harwood Academic Publishers, New York (1983). In press.
10. D. J. Nesbitt and J. T. Hynes, "Vibrational-translational energy transfer from highly excited anharmonic oscillators," *Chem. Phys. Lett.*, vol. 82, p. 252 (1981).
11. D. J. Nesbitt and J. T. Hynes, "Slow vibrational relaxation in picosecond iodine recombination in liquids," *J. Chem. Phys.*, vol. 77, p. 2130 (1982).
12. J. Troe, "Kinetic phenomena in gases at high pressure," in *High Pressure Chemistry*, ed. H. Kelm, pp. 489-520, Reidel (1978).

13. J. M. Zellweger and H. van den Bergh, "The photolytic cage effect of iodine in the gas phase," *J. Chem. Phys.*, vol. 72, p. 5405 (1980).
14. E. G. Marason, "Laser dye DCM: CW, synchronously pumped, cavity pumped and single-frequency performance," *Optics Comm.*, vol. 37, p. 56 (1981).
15. J. Tellinghuisen, "Transition strengths in the visible-infrared absorption spectrum of I_2 ," *J. Chem. Phys.*, vol. 76, p. 4736 (1982).
16. P. Bado, S. B. Wilson, and K. R. Wilson, "Multiple modulation for optical pump-probe spectroscopy," *Rev. Sci. Instrum.*, vol. 53, p. 706 (1982).
17. H. E. Lessing and A. von Jena, "Continuous picosecond spectroscopy of dyes," in *Laser Handbook*, ed. M. L. Stitch, vol. 3, p. 753, North-Holland, Amsterdam (1979).
18. J. P. Bergsma and K. R. Wilson, "Molecular dynamics of chemical reactions in solution: Theoretical dynamics and transient electronic spectra for I_2 photodissociation," *J. Chem. Phys.* (1983). To be submitted.
19. D. L. Bunker and B. S. Jacobson, "Photolytic cage effect, Monte Carlo experiments," *J. Am. Chem. Soc.*, vol. 94, p. 1843 (1972).
20. A. J. Stace and J. N. Murrell, "Molecular dynamics and chemical reactivity. A computer study of iodine atom recombination under high pressure conditions," *Mol. Phys.*, vol. 33, p. 1 (1977).
21. J. N. Murrell, A. J. Stace, and R. Dammel, "Computer simulation of the cage effect in the photodissociation of iodine," *J. C. S. Faraday Transactions II*, vol. 74, p. 1532 (1978).
22. A. H. Lipkus, F. P. Buff, and M. G. Sceats, "Computer simulation of the photodissociation and recombination of iodine in gaseous krypton using a droplet model," *J. Chem. Phys.* (1983). In press.
23. C. L. Brooks and S. A. Adelman, "Dynamics of liquid state chemical reactions: R-dependent correlation functions for $I \cdot + I \cdot$ in CCl_4 ," *J. Chem. Phys.*, vol. 76, p. 1007 (1982).
24. C. L. Brooks III, M. W. Balk, and S. A. Adelman, "Dynamics of liquid state chemical reactions: Vibrational energy relaxation of molecular iodine in liquid solution," *J. Chem. Phys.*, vol. 79, p. 784 (1983).
25. M. W. Balk, C. L. Brooks III, and S. A. Adelman, "Dynamics of liquid state chemical reactions: Photodissociation dynamics and geminate recombination of molecular iodine in liquid solution," *J. Chem. Phys.*, vol. 79, p. 804 (1983).
26. S. A. Adelman, "Chemical reaction dynamics in liquid solution," *Adv. Chem. Phys.*, vol. 53, p. 61 (1983).
27. P. Bado, C. Dupuy, K. R. Wilson, R. Boggy, J. Bowen, and S. Westra, "High efficiency picosecond pulse generation in the 675-930 nm region from a dye laser synchronously pumped by an argon-ion laser," *Optics Comm.*, vol. 46, p. 241 (1983).
28. P. Bado, C. Dupuy, D. Magde, K. R. Wilson, and M. M. Malley, "Molecular dynamics of chemical reactions in solution: Experimental picosecond transient spectra for I_2 photodissociation," *J. Chem. Phys.* (1983). To be submitted.
29. S. J. Rand and R. L. Strong, "Complex formation in the flash photolysis and combination of iodine in benzene," *J. Am. Chem. Soc.*, vol. 82, p. 5 (1960).
30. R. L. Strong, S. J. Rand, and J. A. Britt, "Charge-transfer spectra of iodine atom-aromatic hydrocarbon complexes," *J. Am. Chem. Soc.*, vol. 82, p. 5053 (1960).
31. N. K. Bridge, "Transient species in the flash photolysis of halogens in solution," *J. Chem. Phys.*, vol. 32, p. 945 (1960).

32. R. L. Strong, "The presence of transient charge-transfer complexes in halogen atom recombination and photohalogenation processes," *J. Chem. Phys.*, vol. 66, p. 2423 (1962).
33. S. L. Shostak and R. L. Strong, "Transient absorption following flash photodissociation of halogens in rare gases," *Chem. Phys. Lett.*, vol. 63, p. 370 (1979).
34. J.-C. Dutoit, J.-M. Zellweger, and H. van den Bergh, "The photolytic cage effect of iodine in gases and liquids," *J. Chem. Phys.*, vol. 78, p. 1825 (1983).

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